



Efficient photo-Fenton activity in mesoporous MIL-100(Fe) decorated with ZnO nanosphere for pollutants degradation

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ABSTRACT

Metal-organic frameworks (MOFs) have received significant interest as a promising photocatalyst for environmental remediation due to its high surface area and porous nature. The small pores ($< 2 \text{ nm}$) in microporous MOFs help the adsorption of small molecules but limits diffusion and accessing of bigger molecules from MOF cavities, thus preventing their applications in some situation. The aim of this work is to fabricate mesoporous MOF composite with larger pore sizes ($> 2 \text{ nm}$) and open pore cavities that can provide right pathways for ingoing and outgoing of molecules during catalysis. Herein, we successfully report stable mesoporous MIL-100(Fe) loaded with ZnO NS by an *in situ* self-assembly method. The prepared samples were characterized by Brunauer–Emmett–Teller (BET) and N_2 adsorption–desorption isotherm to study their surface area and porosity. The catalytic performance of mesoporous MIL-100(Fe) was approximately 2–3 order of magnitude more than that of microporous MIL-100(Fe). Such higher catalytic activity in mesoporous MIL-100(Fe) can be ascribed to its mesocellular structure which can improve the molecular diffusion and accessibility inside MOF channels. The charge separation efficiency and photo-Fenton activity of mesoporous MIL-100(Fe) can further be increased by introduction of certain amount of ZnO NS and H_2O_2 . Moreover, the as synthesized sample shows higher photo-Fenton degradation efficiency at lower pH value with certain amount of H_2O_2 . Lastly, the possible catalytic mechanism has been tentatively proposed. This study not only used for the pollutants degradation but also provide useful platform for the application of mesoporous MOFs as an efficient photo-Fenton activity to various other fields.

1. Introduction

Metal-organic frameworks (MOFs) have received significant consideration as a promising candidate for myriad of purposes such as separation, storage and catalysis [1–4]. Their flexible structure have several fascinating properties like high surface area, tunable cavities, tailororable chemistry and thermal stability compared with conventional photo-Fenton like catalyst [5,6]. Pore size distribution in MOFs is of prime importance for the above mentioned applications. However, most of the reported MOFs and related researches so far are limited to microporous regime [7,8] which may inherently limits molecular diffusion and accessing of larger organic molecules to the MOFs cavities, thus reducing the photocatalytic activity in some cases [9,10]. Thereby, it is imperative to solve those issues so as to enhance the photocatalytic activity. Construction of heterostructure and mesoporous MOFs can bring promising pathways to enhance molecular diffusion which could help in mass transport during photocatalytic pollutants degradation

[11]

Besides the difficulties of elongated linkers preparation, poor topologies and disintegration of frameworks almost unavoidably occur in MOFs which avoids these approaches from being commonly adopted in the preparation of mesoporous MOFs [12,13]. Metal-organic frameworks are unstable during soft template process, consequently leading to fragile MOFs [14]. Based on the above challenges, hereby we used unstable metal-organic assemblies (MOAs) as a template to construct stable mesoporous MIL-100(Fe) by an *in situ* self-assembly method [15]. It is well-established that MOF-5 is stable in various reaction solvent [16], the sensitivity towards highly acidic solution ($\text{pH} = 1$) can cause to its structural decomposition [17,18]. Some MOFs are chemically and thermally are very stable, for example MIL-53(Fe), MIL-100(Fe) and UiO-66(Zr) [19,20], which keep their framework stable even in acidic solution. Due to such stability differences, we used acid sensitive MOF (MOF-5) as a potential template to construct mesoporous MIL-100(Fe) [M.MIL-100(Fe) use hereafter]. Iron (III) MOFs can be a

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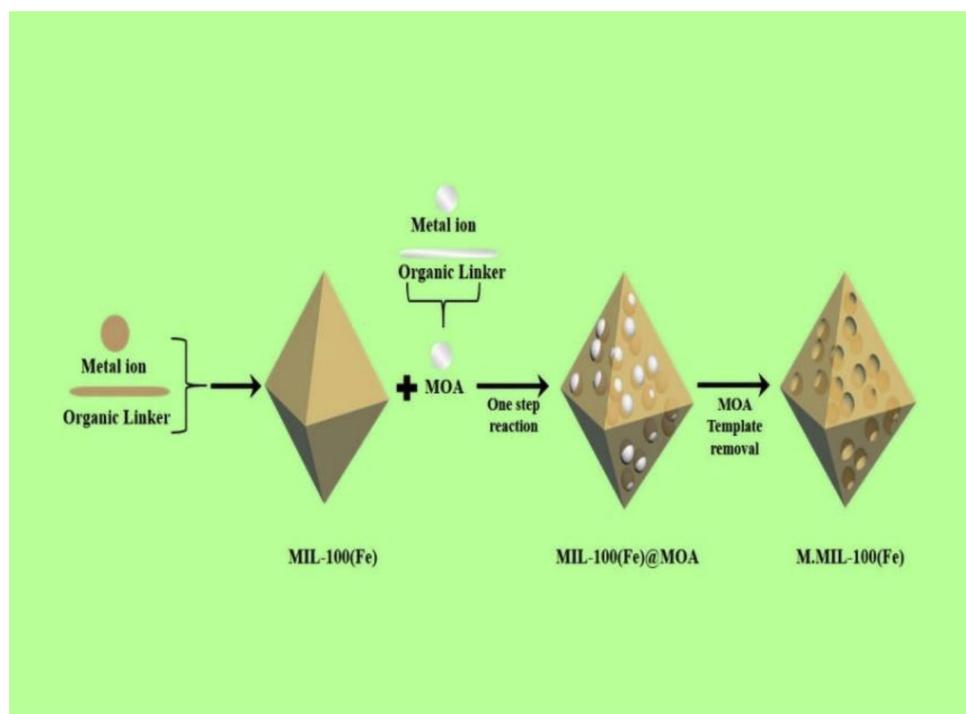


Fig. 1. Schematic diagram for the synthesis of M.MIL-100(Fe).

judicious choice compared to Zr(IV) MOFs for efficient photo-Fenton activity owing to its Fe-metal clusters, low toxicity, suitable band gap (2.7 eV) and more prominently, its firm Lewis acidity makes solid coordination bonds with ligands and thus highly stable framework [21,22].

Despite the great progress in MOFs, there still have low photocatalytic efficiency due to its fast charge recombination and limited light harvesting. Up to now, researchers have been recognized that single component photocatalysts suffer quick charge recombination and thereby limited their photocatalytic activity. To further overcome the charge recombination in MOFs, significant researches have been carried out on metal oxides/MOFs composites [23,24]. Zinc oxide attracted significant attention as a photocatalyst for organic pollutants degradation owing to its non-toxic nature, low cost, high reactivity and significant optical and electrical properties. The previous results shows that ZnO NPs have been successfully distributed on the surface of mesoporous materials [25,26] which shows high catalytic activity. In case of ZnO based composite with porous materials, the kinetics of the degradation was faster than TiO₂. By serving the M.MIL-100(Fe) as a support for ZnO NS, thereby also circumventing the common issue of ZnO aggregation and promoting their application for photocatalytic efficiency. Loading of such material to Fe-MOF structure would be a favorable pathway for the construction of new composites. However, as far as we know, such type of work has not been done previously.

In this study, we synthesized M.MIL-100(Fe) loaded with ZnO NS by facile method. The photo-Fenton activity of newly prepared M.MIL-100(Fe)@ZnO NS hybrid have been evaluated for TOC removal and degradation of organic pollutants, *i.e.* phenol, bisphenol-A and atrazine. M.MIL-100(Fe)@ZnO NS displayed higher degradation efficiency, signifying to its open pore cavities, rich nanoscale channels that can provide right pathways for ingoing and outgoing of molecules, that might assist in reducing the mass transfer problem during catalytic reaction. The low recombination rate and high photo-Fenton activity of M.MIL-100(Fe)@ZnO NS could also be helpful for efficient pollutants degradation. Because the influence of different parameters (pH value and H₂O₂ concentration) on the performance of photo-Fenton activity, additional analysis were investigated to assess the influence of these

factors on pollutants degradation over M.MIL-100(Fe)@ZnO NS.

2. Experimental

2.1. Materials

Commercially available chemicals were used without additional purification. Trimesic acid (H₃BTC), terephthalic acid (H₂BDC) and N, N-dimethylformamide (99.5%) were bought from Aladdin Chemical industry (China). FeCl₃.6H₂O, Zn (NO₃)₂.6H₂O, H₂O₂ (30%), Isopropyl alcohol, Na₂SO₄, polyvinylpyrrolidone (PVP), Ethanol, HCl and T-Butyle alcohol (TBA) were bought from Damao Chemical Factory, Fuyu Chemical Co., Ltd and Bodi Chemical Co., Ltd (Tianjin city, China). Deionized water (18.2 MΩ) was used during analysis.

2.2. Synthesis of samples

2.2.1. Fabrication of MIL-100(Fe)

MIL-100(Fe) was prepared by solvothermal technique as described previously [27]. Typically, FeCl₃.6H₂O (0.270 g, 1 mM) and H₃BTC (0.210 g, 1 mM) were dissolved into 20 mL DMF in 80 mL Teflon liner autoclave. The mixture solution was then sonicated for 5 min, closed in autoclave and heated in an oven at 150 °C overnight. After cooling, the as prepared sample was isolated by centrifugation and washed with DMF and ethanol many times and dried at 60 °C overnight.

2.2.2. Fabrication of M.MIL-100(Fe)

M.MIL-100(Fe) have been prepared by an *in situ* self-assembly approach with some modification described by Huang et al. [15] as shown in schematic diagram Fig. 1. Briefly, FeCl₃.6H₂O (0.135 g, 0.5 mmol), Zn(NO₃)₂.6H₂O (0.1480 g, 0.5 mM) and organic linkers (0.5 mM) were dissolved into 20 mL DMF in 80 mL Teflon liner autoclave. The mixture solution was then sonicated, sealed and put in oven at 150 °C for 12 h. After cooling at normal temperature, the as synthesized sample was obtained by centrifugation and washed three times with acetone and DMF. The powder was then dispersed in HCl solution (pH = 1.0) and stirred about 5–10 min to destroy metal-organic assembly template. The

final product was isolated by centrifugation and washed again three times with DMF and acetone to remove the decomposed template and dried it for overnight at 70 °C.

2.2.3. Preparation of ZnO nanosphere

ZnO NS was prepared by the method as described by Wang et al. [28]. Briefly, into a 50 mL diethylene glycol, 1.09 g Zn(O₂CCH₃)₂ was added and stirred at 160 °C for 1 h. After cooling at normal temperature, a white sample was isolated through centrifugation and washed two times by ethanol.

2.2.4. Preparation of M.MIL-100(Fe)@ZnO nanosphere

M.MIL-100(Fe)@ZnO NS hybrid was prepared using a facile technique as described by Liang et al. [8]. To be specific, M.MIL-100(Fe), ZnO NS (25%wt.), polyvinylpyrrolidone (0.0333 g), H₂O (12 mL) and ethanol (3 mL) were mixed together in 150 mL beaker. The mixture was then refluxed at 90 °C and kept on this temperature for 3 h. The sample was achieved after washing several times with ethanol and dried in oven at 60 °C for 4 h.

2.3. Characterizations

The powder X-ray diffraction (XRD) measurement of the samples were carried out on EMYPREAN diffractometer with monochromatized Cu K α radiation ($k = 1.5418 \text{ \AA}$) over a 2 theta degree of 5°–80°. The morphology images of the samples were obtained by scanning electron microscopy (SEM, S-4800), transmission electron microscopy (TEM, FEI Company, USA) and high resolution transmission electron microscopy (HRTEM). The Brunauer-Emmett-Teller (BET) surface area, nitrogen adsorption-desorption isotherm and porosity distribution were studied through Quantachrome SI (USA) at 77 K. The elemental valence state and surface chemical environment were determined by X-ray photo-electron spectroscopy (XPS). UV-vis diffuse reflectance spectroscopy of as prepared samples were recorded through UV-vis spectrophotometer (UV-2450, Japan). Barium sulfate was used as a standard of reflectance. Photoluminescence (PL) spectroscopy was conducted on a Hitachi F-4500 spectrometer with a wavelength of 340 nm. The transient photocurrent and Mott-Schottky test were achieved on photo electrochemical workplace (CHI 650B, CH instruments Inc., Shanghai) with an electrolyte solution of Na₂SO₄ (0.2 M), using three electrodes system; i.e. modified ITO glass, Pt foil and saturated calomel electrode as working, counter and reference electrode respectively. Leached iron during photocatalytic degradation reaction was conducted on inductively coupled plasma optical emission spectroscopy (ICP, Perkin Elmer Optima 2000 USA).

2.4. Photocatalytic experiment

Photocatalytic activity of as synthesized samples were tested for phenol, bisphenol A and atrazine degradation, which were conducted in 80 mL cylindrical Pyrex vessel reactor by using LSH-500 W Xe arc lamp as a light source. To be specific, 0.01 g catalyst was mixed with 50 mL of 5 mg L⁻¹ phenol, bisphenol A and atrazine aqueous solutions. The pH of the suspension (pH = 2) was fixed by mixing certain amount of HCl with aqueous solution. Before exposed to visible light irradiation, the solution was stirred to reach adsorption-desorption equilibrium for about 1 h. To increase photo-Fenton activity, certain amount of H₂O₂ was mixed into the above suspension and the light was turned on. The suspension was evenly stirred during photodegradation reaction. As the reaction proceeded, 1 mL samples from a solution were taken at fixed interval (20 min) and filtered through 0.22 μm membrane filter. After each pollutant degradation, the photocatalyst was reused after washing with water and ethanol. The active species trapping experiment was conducted by using TBA as ·OH scavenger. The photocatalytic pollutants degradation over M.MIL-100(Fe)@ZnO NS under various reaction conditions like initial pH value and H₂O₂ concentration were also

carried out.

2.5. Analytical method

The high performance liquid chromatography analysis (HPLC Agilent 1200) analysis was used to measure the pollutants degradation. Water-methanol (70:30, v/v) mixture was used as a mobile phase for both phenol and bisphenol-A with a wavelength detection of 270 nm and 280 nm respectively. Water-acetonitrile (50:50 v/v) mixture solution was used as a mobile phase for atrazine with a wavelength detection of 220 nm. The total organic carbon (TOC) removal was tested by using multi N/S 2100S (analytikjena, Germany). Electron paramagnetic resonance (EPR) experiment was used to detect the reactive oxidative species. The signals of the trapped radicals were tested on Bruker 300E spectrometer (Germany) at ambient temperature. The DMPO-radical adduct was prepared by dissolving 1 mL sample (10 mg + appropriate amount of water) into 20 μL (0.1 M DMPO) and then were added in a cylindrical quartz cell (100 mm in length and 2 mm in diameter). UV-vis light (420 nm cutoff filter) was used as a source of light. The signal was obtained in every 2 min.

3. Results and discussion

3.1. Characterization

X-ray power diffraction (XRD) measurements were performed as shown in Fig. 2. Both MIL-100(Fe) and M.MIL-100(Fe) display well defined and high diffraction peaks indicating its well crystallinity which is similar to XRD pattern as reported previously [8,29]. The structures of both MIL-100(Fe) and M.MIL-100(Fe) were unchanged after acid treatment indicating its good chemical stability. Additional characteristic peaks of ZnO were observed in case of M.MIL-100(Fe)@ZnO NS, showing successful dispersion of ZnO NS on M.MIL-100(Fe). ZnO NS peaks are good corresponding to the hexagonal wurtzite structure (P6₃mc, $a = 3.2495 \text{ \AA}$, $c = 5.2069 \text{ \AA}$, JCPDS no. 36-1451) of ZnO. There is no shift in the peak position of M.MIL-100(Fe), indicating that ZnO NS did not influence its crystal structure.

The morphology of the samples were examined by SEM and TEM as shown in Fig. 3. SEM images show that small hexagonal morphology (Fig. 3A) of MIL-100(Fe) and rod like structure (Fig. 3B) for M.MIL-100(Fe) was obtained; indicating that acid treatment greatly influenced the morphology. The magnified SEM image in Fig. 3C demonstrates that smaller spherical ZnO nanoparticles loaded on the surface of M.MIL-100(Fe). Fig. 4 shows TEM and HRTEM images of M.MIL-100(Fe)@ZnO NS. These images further confirmed the successful synthesis of M.MIL-

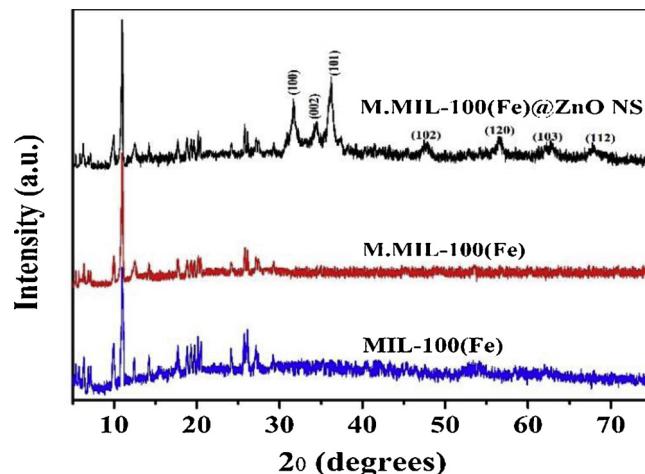


Fig. 2. XRD pattern of MIL-100(Fe), M.MIL-100(Fe) and M.MIL-100(Fe)@ZnO NS.

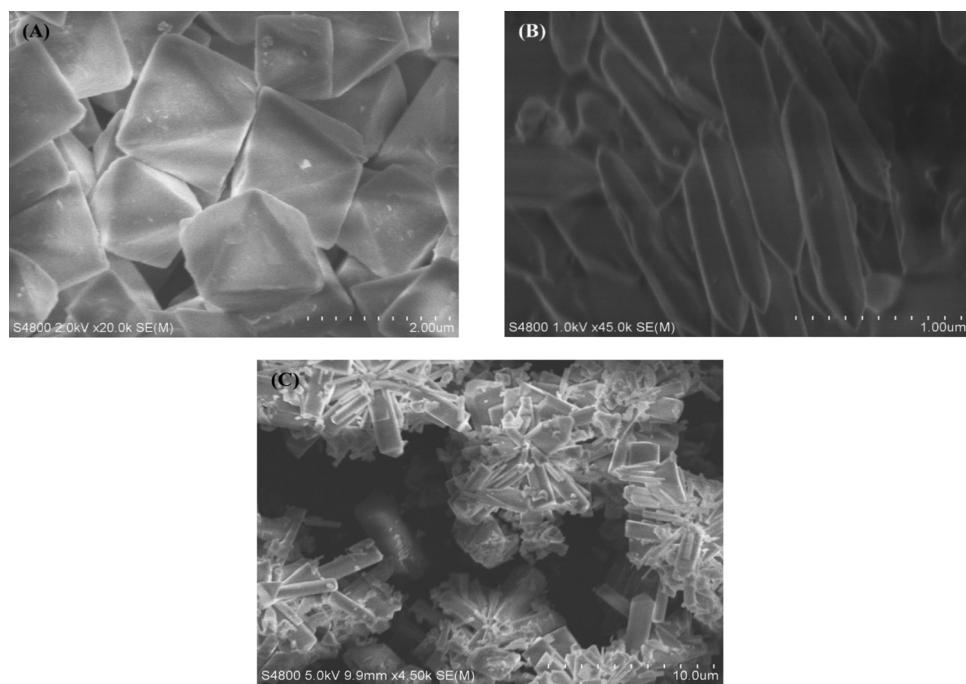


Fig. 3. SEM images of pristine MIL-100(Fe) (A), M.MIL-100(Fe) (B) and M.MIL-100(Fe)@ZnO NS (C).

100(Fe)@ZnO-. HRTEM image in Fig. 4B clearly shows that ZnO NS dispersed on M.MIL-100(Fe) displays distinct fringes. Fringes with $d = 0.28$ nm could be described as the (100) plane of ZnO NS. Successful loading of ZnO NS on M.MIL-100(Fe) could be associated with high surface area and porous nature of M.MIL-100(Fe). Additionally, the protection of PVP is strong enough around ZnO NS so that its self-aggregation is inhibited greatly during synthesis.

To probe the elemental composition and binding position of M.MIL-100(Fe)@ZnO NS, X-ray photoelectron spectroscopy (XPS) measurement was used. Typical survey XPS in Fig. 5A verified the presence of C, Fe, Zn and O elements in M.MIL-100(Fe)@ZnO NS. Fe 2p spectrum are split into two well-defined Fe2p_{3/2} and Fe 2p_{1/2} peaks (Fig. 5B) at the binding energies of 712.2 and 726.1 eV respectively. These two peaks are attributed to the Fe(III) metals in M.MIL-100(Fe). The separation of peaks, specifically, $\Delta = \text{Fe } 2\text{p}_{1/2} - \text{Fe } 2\text{p}_{3/2} = 14.1$ eV, that is in agreement with Yu et al. [30]. For O 1 s spectra in Fig. 5C, two well-defined peaks are separated at binding energies of 531.5 and 532.1 eV which are associated with oxygen element in the Fe-O and BTC ligands respectively. The high resolution XPS of C 1 s in Fig. 5D split into two distinct peaks, which are associated with benzene ring (284.4 eV) and carboxylic functional group (288.5 eV). Observation of Zn 2p spectrum presents two characteristic peaks at a binding range of 1021.5 and 1045 eV, which can be assigned to the existence of ZnO on the surface of M.MIL-100(Fe) (Fig. 5E).

To estimate the photoexcited performance of M.MIL-100(Fe)@ZnO NS, we first measured optical properties by using UV-vis DRS (Fig. 6). All samples shows strong characteristics absorption at 360 nm that could be associated with ligands-to-clusters charge transfer (LCCT) mechanism, suggesting the strong bonding of ligands oxygen with Fe (III) atom [31]. Furthermore, small peaks positioned at about 470 nm could be attributed to the transition ($^6\text{A}_{1g} = > ^4\text{A}_{1g} + ^4\text{Eg(G)}$) in Fe (III) [32]. It was found that after introduction of ZnO NS, M.MIL-100(Fe)@ZnO NS exhibited more strong absorption spectra in both visible and UV region, which could be due to the excitation of ZnO NS at wavelength below 380 nm [33]. Such boosted optical absorption would bestow to M.MIL-100(Fe)@ZnO NS with more chance of utilization of incident light to formed more active species for efficient photocatalytic activity. Clearly, such high photogenerated carriers and their efficient separation may further enhance photocatalytic performances. The band gap energy (Eg) was calculated from DRS data using Tauc plots method and based on relation of $Eg = 1240/\lambda$ [34] as shown in supporting information (Fig. S1A and B).

$$K(hv - Eg)/n = F(R) h\nu$$

F (R) and K is the coefficient of absorption and constant respectively, while n is calculated from optical transition. M.MIL-100(Fe) shows typical DRS agreeing to the previous reports with absorption edge at

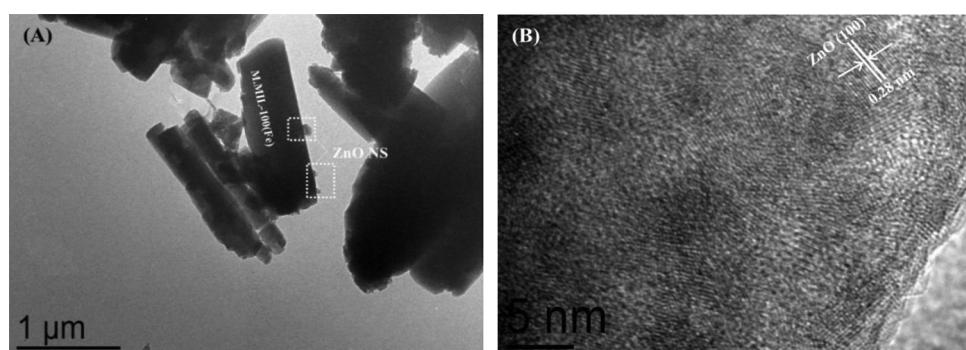


Fig. 4. TEM (A) and HRTEM (B) images of M.MIL-100(Fe)@ZnO NS.

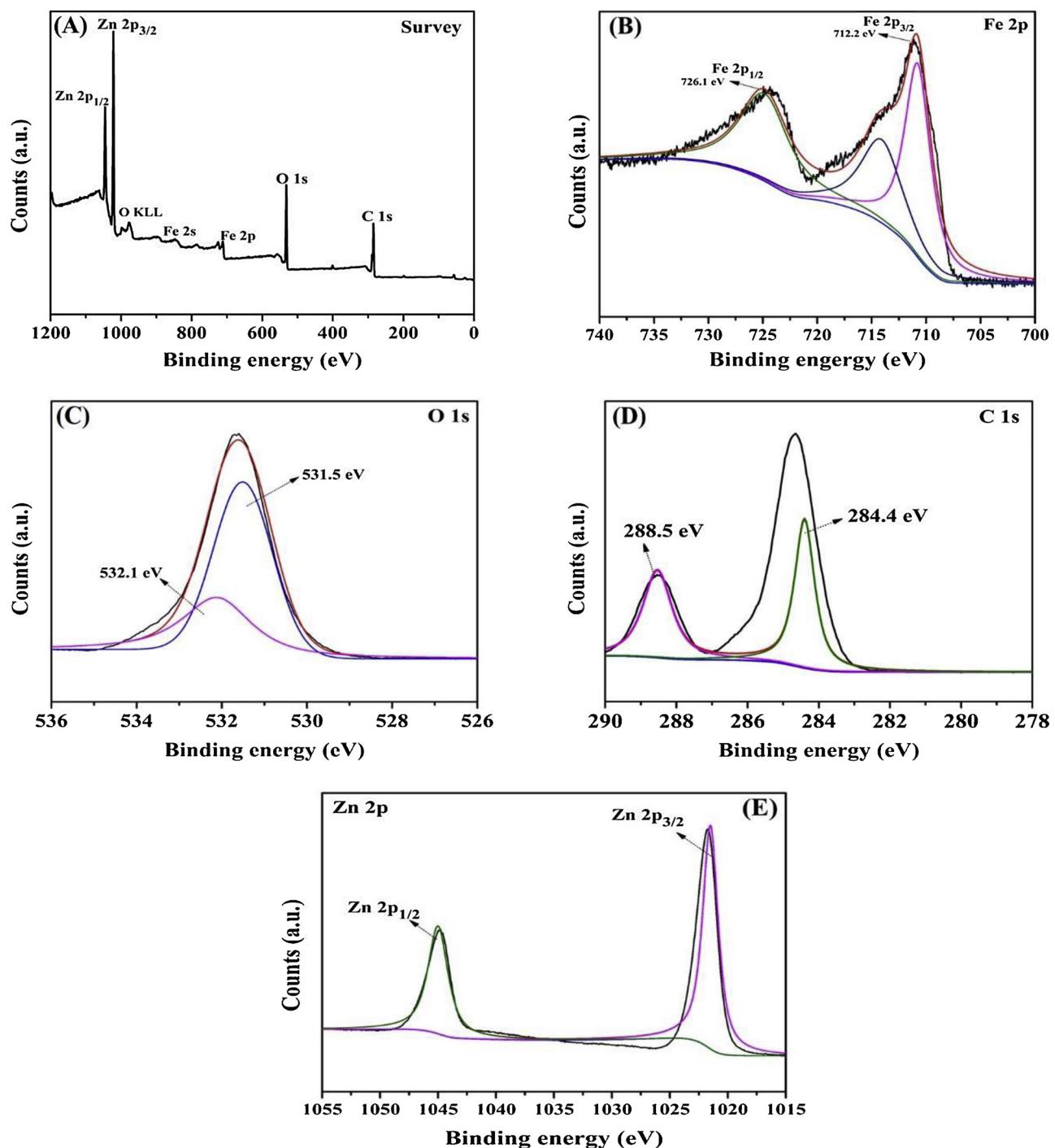


Fig. 5. XPS spectra of M.MIL-100(Fe)@ZnO NS: Survey (A), Fe 2p (B), O 1s (C), C 1s (D) and Zn 2p (E).

wavelength of 472 nm, agreeing with the optical gap energy of 2.63 eV.

To probe the photoexcited charge separation, we investigated the transient photocurrent performance of as prepared M.MIL-100(Fe)@ZnO NS. Fig. 7A presents photocurrent versus time (I-t) curve of as synthesized samples with off and on rotations of visible light irradiation. Obviously, all the samples display rapid in photocurrent density. M.MIL-100(Fe)@ZnO NS shows better photocurrent behavior compared to pristine MIL-100(Fe). By encapsulation with ZnO NS, the photocurrent density of resulting M.MIL-100(Fe)@ZnO NS further increased, signifying that longer period, low recombination and more efficient separation of photoinduced charge carrier. The photocurrent density of M.MIL-100(Fe)@ZnO NS is approximately 3 times higher (1.19×10^{-6} A

cm^{-2}) than that of pristine MIL-100(Fe) (3.71×10^{-7} A cm^{-2}). It can further be proved from photoluminescence (PL) analysis as shown in Fig. 7B. Energy is released due to electron-hole pair's recombination, which can be identified by photoluminescence (PL) spectra. PL spectra of M.MIL-100(Fe)@ZnO NS was attained at normal temperature at 340 nm wavelength. A lower PL intensity indicates the lower charge carrier recombination. Compared to MIL-100(Fe), M.MIL-100(Fe) and M.MIL-100(Fe)@ZnO NS shows much lower PL intensities. M.MIL-100(Fe) shows strong PL spectra at 468 nm which could be attributed to organic linkers [8]. The introduction of ZnO NS on M.MIL-100(Fe) surface could diminish the PL intensity, suggesting the recombination inhibition and longer life time of photoinduced charge carriers.

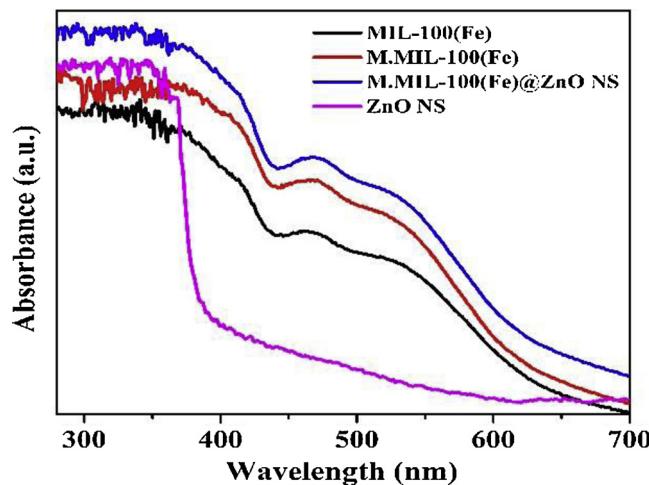


Fig. 6. UV-vis light DRS of M.MIL-100(Fe)@ZnO NS.

3.2. BET and porosity distribution analysis

Stable mesoporous MIL-100(Fe) have been created using unstable metal organic assembly by an *in situ* self-assembly methodology. Metal-organic assembly (MOF-5) used as a template to prepare mesoporous MIL-100(Fe) due to its structural decomposition and collapse in acid solution. After removal of template by acid treatment, N_2 adsorption-desorption isotherm was confirmed the mesoporous MIL-100(Fe). BET surface area and porosity distributions were tested to described the porosity as shown in Fig. 8. MIL-100(Fe) shows concave curve to the relative pressure (P/P_0), which exhibits typical type 1 isotherm, a solid proof of microporous structure [35]. Both M.MIL-100(Fe) and M.MIL-100(Fe)@ZnO NS shows hysteresis loop as shown in Fig. 8A, that is attributed with the capillary condensation occurs in mesoporous structure. Both samples shows typical type IV isotherm, an indication of mesopores structure [15]. Loading of ZnO NS, a little bit decreased in the surface area and pore width of M.MIL-100(Fe)@ZnO NS, which could be attributed to the pore blockage by some ZnO nanoparticles. BET surface area of MIL-100(Fe), M.MIL-100(Fe) and M.MIL-100(Fe)@ZnO NS is 730, 766 and $654\text{ m}^2\text{ g}^{-1}$ with pore diameter of 14.1, 35.3 and 35.1 Å and pore volume of 0.17, 0.37 and $0.36\text{ cm}^3\text{ g}^{-1}$ respectively as shown in Fig. 8B and Table 1. The upsurge in surface area of M.MIL-100(Fe) could be associated with thoroughly removal of guests and other organic solvent molecules from the pores of M.MIL-100(Fe) during the washing and reflow process.

3.3. Photocatalytic activity

Phenol, bisphenol A and atrazine were taken as model pollutants for photo-Fenton degradation over M.MIL-100(Fe)@ZnO NS nanocomposite. Fig. 9A shows phenol degradation over different catalysts in the present visible light ($\lambda \geq 420\text{ nm}$). An insignificant phenol degradation is found in dark condition (curve a). The degradation efficiency is marginally increased by the addition of H_2O_2 probably due to its photolysis under visible light condition (without catalyst, curve b). In the absence of H_2O_2 , the degradation efficiency increased over pristine MIL-100(Fe) and M.MIL-100(Fe) (curve c and d). Comparatively higher activity of M.MIL-100(Fe) could be associated with its open pore channels and mesocellular structure which can enhance molecular diffusion [36,37]. It was found that after introduction of ZnO NS, phenol degradation further increased, which could be attributed with efficient charge separation and low recombination rate in mesoporous MOF composite. Notably, almost 95% phenol was removed in the presence of M.MIL-100(Fe)@ZnO NS and H_2O_2 within 120 min of visible light irradiation, indicating its efficient photo-Fenton activity. For further confirmation about higher photocatalytic performance of M.MIL-100(Fe)@ZnO NS + H_2O_2 , we also performed the activity test on bisphenol A (Fig. 9B) and atrazine (Fig. 9C). Apparently, the M.MIL-100(Fe)@ZnO NS shows highest photocatalytic degradation of bisphenol A and atrazine with similar experimental condition. As shown in Fig. 10 that 43–49% TOC was degraded in the M.MIL-100(Fe)@ZnO photo-Fenton like system within 120 min of visible light irradiation, which is higher than conventional MIL-100(Fe) (less than 30%).

The result demonstrates that construction of heterostructure and mesoporous Fe-MOFs composite is important to get sufficient higher performance in photo-Fenton like pollutants degradation. Creation of mesopores with open pore cavities let the reactants to easily diffuse to interior media and allow external and internal surfaces for entirely contact with the reactants. Furthermore, Fe in the mesoporous Fe-MOFs would accelerate the H_2O_2 decomposition to produce $\cdot OH$ radicals. Certain amount of ZnO NS was loaded on mesoporous MIL-100(Fe) to lower the electron-hole recombination during photo-Fenton reaction.

To assess the effect of initial pH value and H_2O_2 concentration, additional analysis were carried out. A rapid degradation was found at initial stage followed by slow decay stages under various reaction parameters. The rapid degradation at first 20 min can be described by abundant amount of Fe in mesoporous MIL-100(Fe) and high concentration of H_2O_2 in the suspension. In this situation, Fe in open pore cavities as well as on the surface of M.MIL-100(Fe) might react with the neighboring H_2O_2 , generating sufficient quantity of $\cdot OH$ radicals with incidence of visible light. Due to the fast consumption of H_2O_2 and Fe clusters at the initial stage, the degradation rate little bit slows down after 20 or 30 min. Similar research phenomena were also found in other works [11,38].

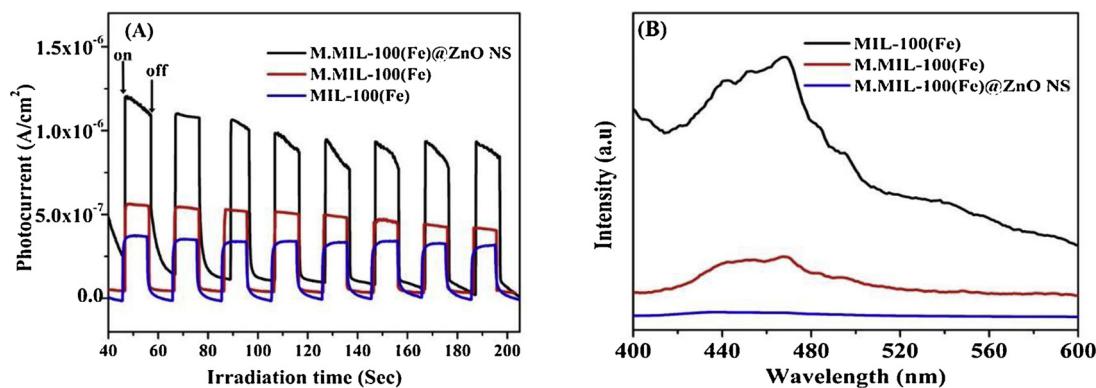


Fig. 7. Transient photocurrent (A) and photoluminescence response (B) of MIL-100(Fe), M.MIL-100(Fe) and M.MIL-100(Fe)@ZnO NS in 0.2 M Na_2SO_4 solution in the presence of visible light.

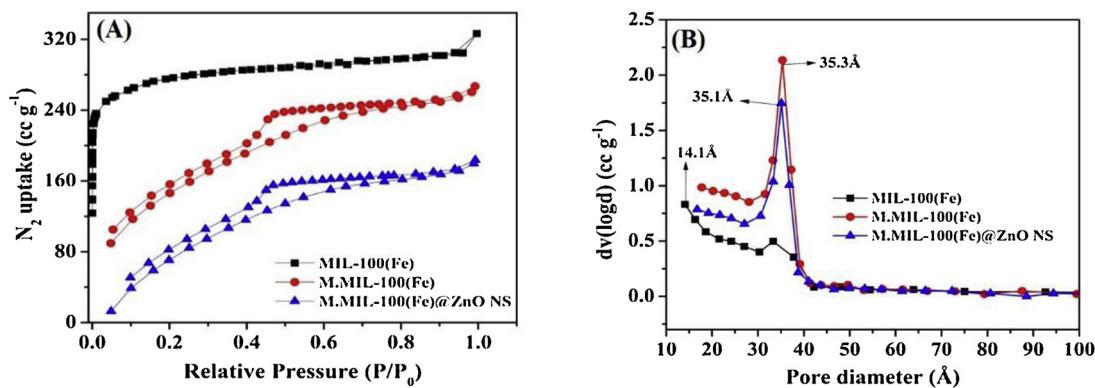


Fig. 8. The N_2 adsorption-desorption isotherms (A) at 77 K and pore size distribution plots (B) of as synthesized samples.

Table 1
BET and pore features of as prepared samples.

Samples	BET Surface area ($\text{m}^2\text{ g}^{-1}$)	Pore volume ($\text{cm}^3\text{ g}^{-1}$)	Pore width (\AA)
MIL-100(Fe)	730	0.17	14.1
M.MIL-100(Fe)	766	0.37	35.5
M.MIL-100(Fe)@ZnO NS	654	0.36	35.3

Figs. 11–13 and S2–S4 shows the effect of various parameters on photo-Fenton pollutants degradation by M.MIL-100(Fe)@ZnO NS. It was found the degradation efficiency decreased obviously from 92 to 68% (taken mean value for all three pollutants) and reaction rate constant (k) value reduced from 0.0341 to 0.0144 min^{-1} (phenol), 0.0334 to 0.0123 min^{-1} (bisphenol A) and 0.0142 to 0.0071 min^{-1} (atrazine) with increase initial pH value from 2 to 7. The decrease in pollutants removal efficiency could be associated with auto decomposition of H_2O_2 [39,40] and water and also poor $\cdot\text{OH}$ oxidation potential at higher pH (2.8 V at pH = 0 and 1.9 V at pH = 7.0) [41].

Figs. 11B–13 B and S2–S4B, shows the influence of various

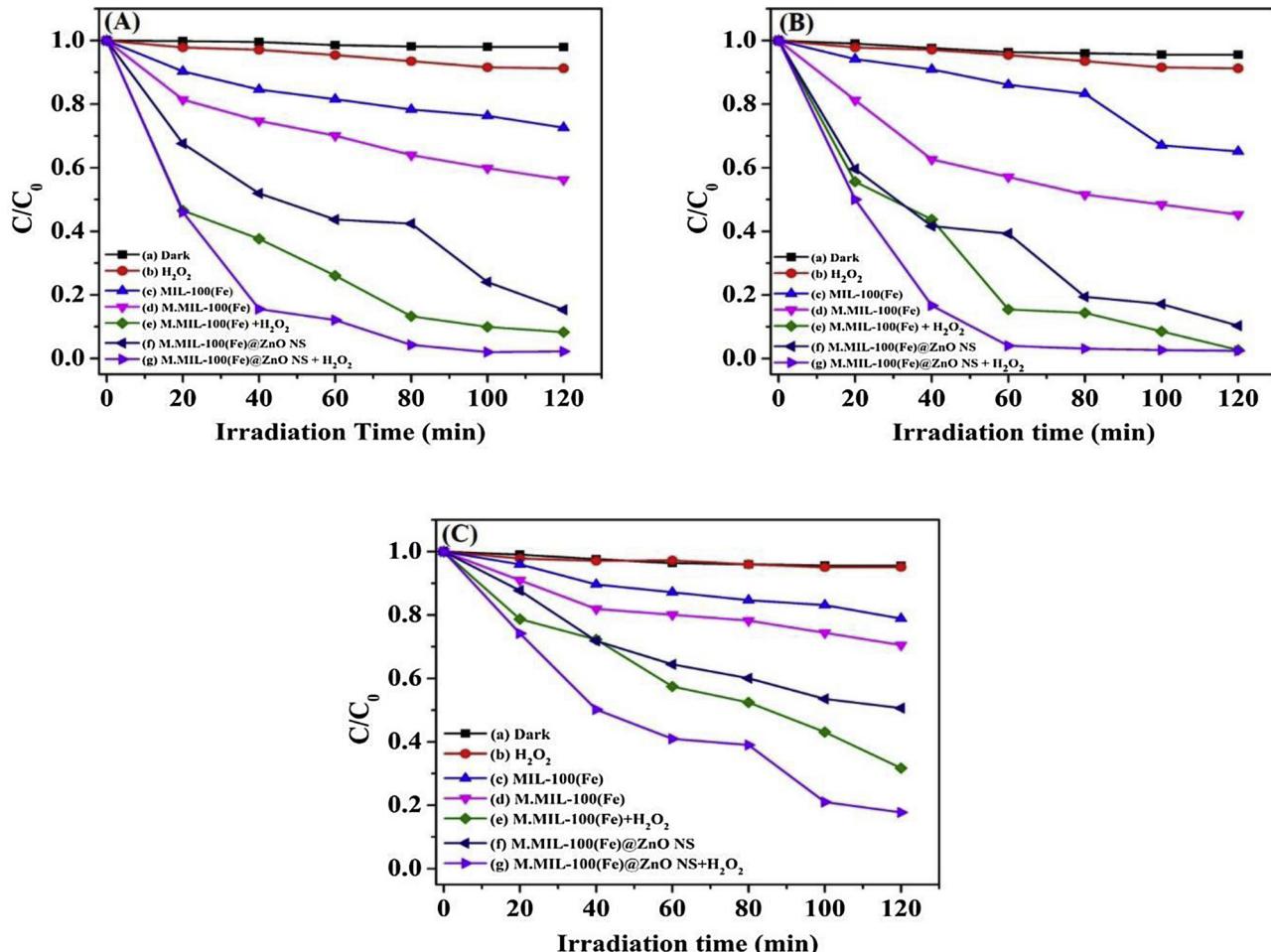


Fig. 9. Degradation of phenol (A), biphenol A (B) and atrazine (C) under visible light irradiation. Except for the studied parameter, other parameters remain constant like: pH 2.0, H_2O_2 concentration = 10 mM. Catalyst = 0.2 g/L.

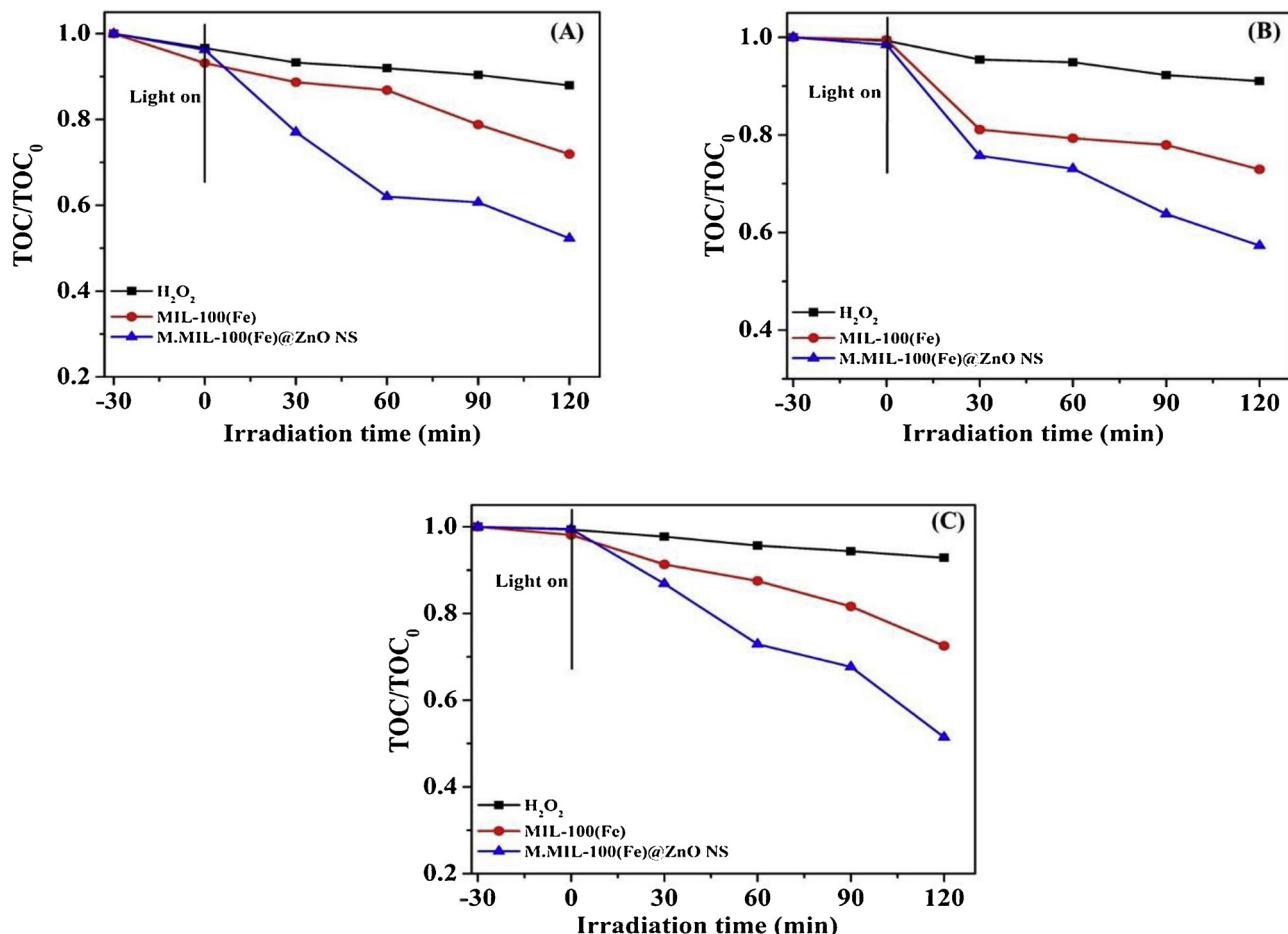


Fig. 10. TOC removal of phenol (A), biphenol A (B) and atrazine (C) under visible light irradiation. Reaction condition: pH 2.0, H_2O_2 concentration = 10 mM. Catalyst = 0.1 g/L.

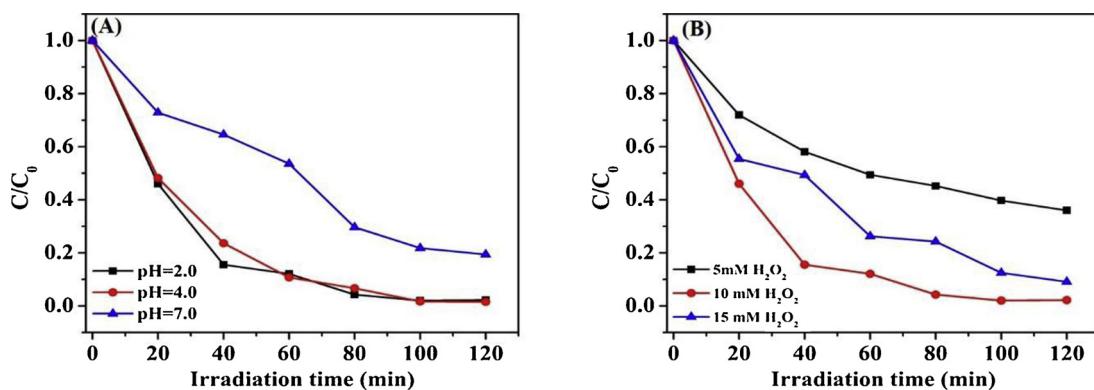


Fig. 11. Degradation of phenol under different parameters: pH (A) and H_2O_2 (B).

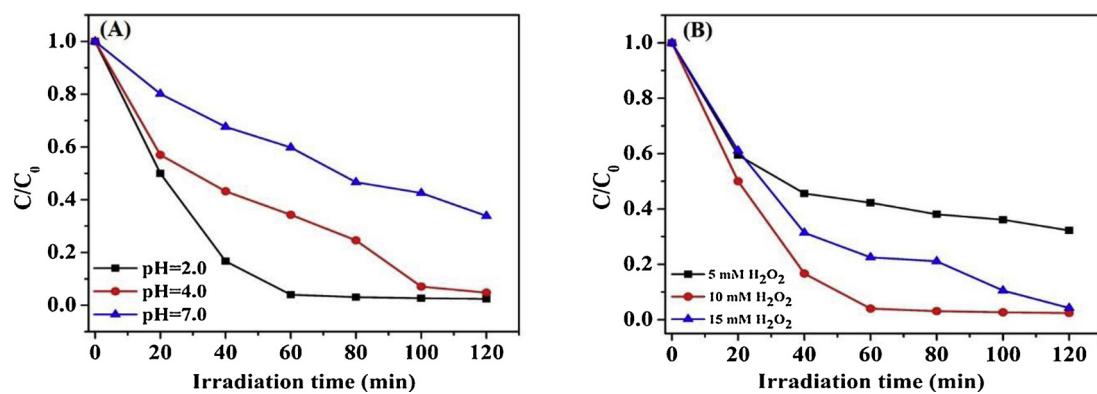
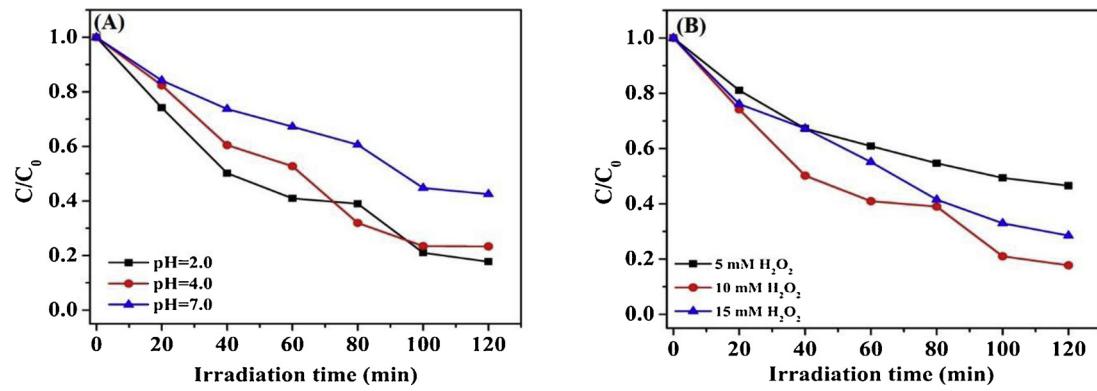
concentration of H_2O_2 on photo-Fenton degradation. By the increase in the concentration of H_2O_2 from 5 to 10 mM, the pollutants degradation efficiency enhanced from 55 to 92% (taken the mean value of all three pollutants) and the reaction rate constant (k) increased from 0.0080 to 0.0339 min^{-1} (phenol), 0.0081 to 0.0334 min^{-1} (bisphenol A) and 0.0062 to 0.0142 min^{-1} (atrazine). Such increase in the degradation efficiency could be probably generation of more $\cdot\text{OH}$ radicals during photo-Fenton activity. However, further increase in the concentration of H_2O_2 up to 15 mM, the degradation activity decreased to 86% and the reaction rate constant (k) value also decreased. It can be clarified that additional H_2O_2 could acts as $\cdot\text{OH}$ scavenger to form perhydroxyl radical ($\cdot\text{HO}_2$) whose oxidation potential is low as described in Eqs. (1)

and (2) [42,43].



3.4. Stability and reusability

Five times recycling experiment was performed to probe the durability of M.MIL-100(Fe)@ZnO NS photocatalyst. The solid catalyst was regenerated after washing with ethanol and water to fully eliminate the adsorbed pollutants. As shown in Fig. 14A that after five time recycling

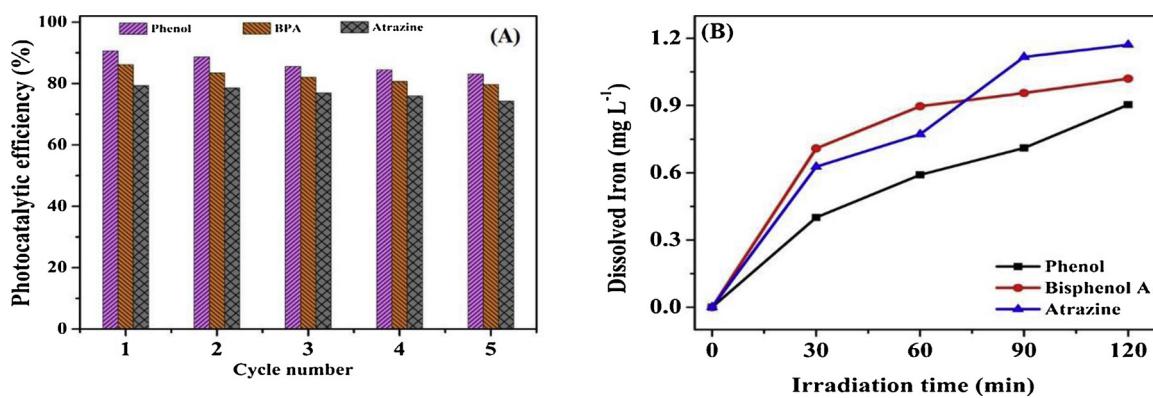
Fig. 12. Degradation of bisphenol A under different parameters: pH (A) and H_2O_2 (B).Fig. 13. Degradation of atrazine under different parameters: pH (A) and H_2O_2 (B).

experiment, the photo-Fenton performance of M.MIL-100(Fe)@ZnO NS does not apparently decreased, indicating that M.MIL-100(Fe)@ZnO NS possess excellent stability in aqueous solution. Furthermore, the concentration of leached Fe(III) ions has been investigated by inductively coupled plasma (ICP) optical emission spectroscopy. The results in Fig. 14B show that only small amount of iron leaching occurred within 120 min visible light reaction. The highest amount of leached iron is found as 1.17 mg L^{-1} during atrazine degradation, which is also less than an environmental standard (2 mg L^{-1}). The result is reasonable by considering the facts that MOFs are sensitive to aqueous solution.

3.5. Reactive oxidative species (ROS) and charge separation mechanism

To study the reactive oxidative species (ROS) generated during photo-Fenton activity were measured by DMPO-trapped electron

paramagnetic resonance (EPR) technique. The stronger the EPR spectra, the larger generation of 'OH amount. Due to hyperfine contact between N atom of DMPO and electron spin of 'OH, the EPR spectra divided into four peak lines. With the addition of H_2O_2 along with catalyst under visible light irradiation, the characteristics four-fold spectrum of DMPO-'OH adduct with intensity ratio of ca. 1:2:2:1 was found, suggesting photocatalytic potential of as prepared sample. However, very weak DMPO-'OH spectrum was observed in case of H_2O_2 only. The amount of generated 'OH follows the order of $H_2O_2 + \text{catalyst} + \text{light} > H_2O_2 + \text{catalyst} > H_2O_2$ as shown in Fig. 15A. Thus, its concluded 'OH radicals is the key ROS responsible for the organic pollutants degradation over M.MIL-100(Fe)@ZnO NS. Furthermore, we measured the effect of 'OH on pollutants removal efficiency by using TBA as 'OH scavenger. The degradation efficiency of M.MIL-100(Fe)@ZnO NS reduced from 92 to 30% within 120 min of

Fig. 14. Reusability test (A) of M.MIL-100(Fe)@ZnO and leached iron concentration with the passage of time (B) during the degradation of phenol, bisphenol A and atrazine. Reaction condition: pH = 2, $[H_2O_2] = 10 \text{ mM}$, [catalyst] = 0.2 g L^{-1} .

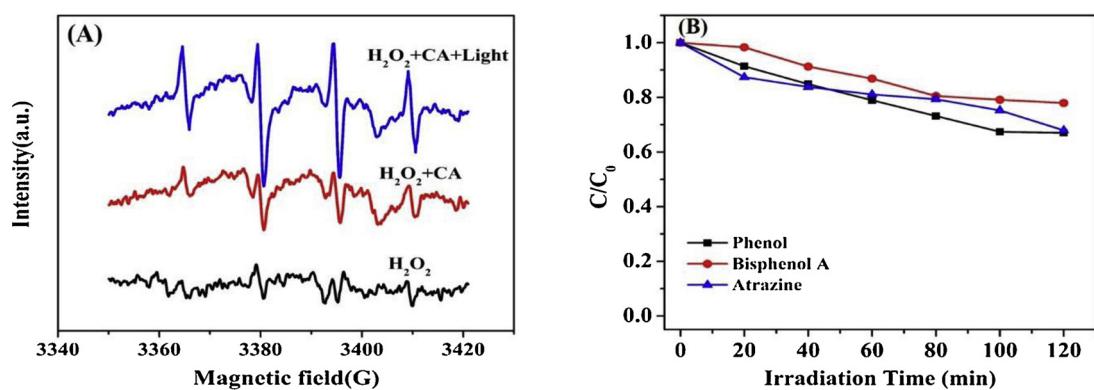


Fig. 15. DMPO-trapped electron paramagnetic resonance (EPR) spectra over M.MIL-100(Fe)@ZnO NS in different conditions (A) and the pollutants degradation on M.MIL-100(Fe)@ZnO NS with incidence of visible light in the co-existence of 50 mM TBA as ·OH scavenger (B).

irradiation by the addition of 50 mM TBA as depicted in Fig. 15B. Such hinder effect of TBA further specifies that ·OH is the main reactive oxidative species and play a major part in the degradation of pollutants.

Furthermore, Mott-Schottky test have been measured in dark presented in Fig. S5. The flat band of M.MIL-100(Fe) and ZnO was measured from Mott-Schottky plot which is estimated to be -0.60 and -0.16 V vs HgCl corresponding to the potential of -0.36 and -0.08 V versus NHE respectively. The energy band gap calculated from DRS for both M.MIL-100(Fe) and ZnO NS, the valence band (VB) potential are estimated to be 2.27 and 3.13 V vs. NHE respectively. The corresponding band gap between ZnO NS and M.MIL-100(Fe) realized it hypothetically possible of moving electron from the conduction band (CB) of M.MIL-100(Fe) to the CB of ZnO NS under the incident of visible light, resulting excellent photoinduced charge separation. This is also evidenced from transient photocurrent and photoluminescence response.

According to results and discussion discussed above, a thorough

charge separation mechanism of over M.MIL-100(Fe)@ZnO NS composite have been postulated in the scheme as shown in Fig. 16. Electron-hole pairs generates by ligand-to-cluster charge transfer or by the direction excitation of the Fe-O clusters [31,32]. It is recognized that charge exchange occurs between MOF and inorganic semiconductor which considerably prevents the charge recombination during catalysis. Concerning M.MIL-100(Fe)@ZnO NS, the holes (h^+) are produced in the VB of M.MIL-100(Fe) due to moving of excited electrons from the VB to CB. The excited electrons move from CB of M.MIL-100(Fe) to CB of ZnO NS by their contact which decreased the electron-hole recombination. Similarly holes (h^+) in the VB of M.MIL-100(Fe) can react with $\text{H}_2\text{O}/\text{OH}^-$ to generate ·OH radicals.

On the other hand, introduction of H_2O_2 could serve as an efficient scavenger that could also accept photoexcited electron to form more ·OH radicals as shown in Eq. (3). Furthermore, H_2O_2 can decomposed by the reaction with Fe(III) metals of M.MIL-100(Fe), produced additional ·OH radicals, so increasing photo-Fenton activity. As generally

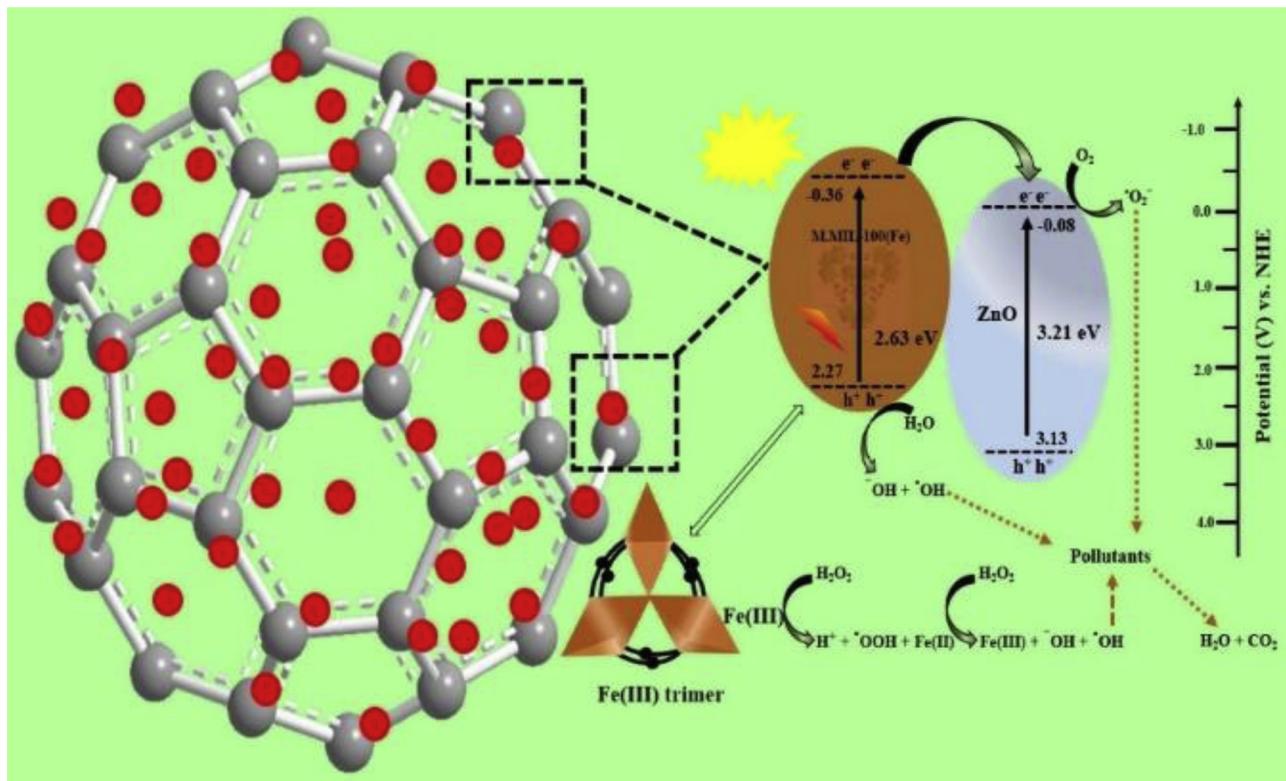
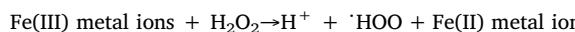
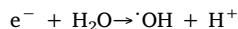
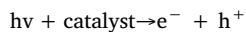


Fig. 16. Mechanistic scheme of photo-Fenton reaction over M.MIL-100(Fe)@ZnO NS hybrid for phenol, bisphenol A and atrazine degradation.

accepted, that in heterogeneous and homogeneous fenton like reaction, the exchanging of electron between Fe(II)/Fe(III) and H₂O₂ encourages the generation of ·OH radicals.



The generated surface Fe(II) react with H₂O₂ to produce ·OH.



Finally organic pollutants were decomposed by ·OH.



4. Conclusion

In summary, we synthesized a highly reactive visible light response M.MIL-100(Fe) photocatalyst by an *in situ* self-assembly template approach and successfully loaded with ZnO NS on M.MIL-100(Fe). The prepared catalyst was then implemented for the degradation and TOC removal of phenol, bisphenol A and atrazine. M.MIL-100(Fe)@ZnO NS exhibits remarkable photo-Fenton activity towards the degradation of phenol, bisphenol A and atrazine and removal of TOC in contrast to conventional MIL-100(Fe) and ZnO individually. The higher activity of M.MIL-100(Fe) could be associated with mesocellular structure and open pore cavities that let the reactants to easily diffuse to interior media and allow external and internal surfaces for entirely contact with the reactants. Furthermore, Fe in mesoporous MOF would increase H₂O₂ decomposition to produce more ·OH radicals to enhance photo-Fenton activity. ZnO NS were loaded on mesoporous MIL-100(Fe) to lower the electron-hole recombination. The photo-Fenton degradation over M.MIL-100(Fe)@ZnO NS were found to be dependent on various factors like initial pH value and H₂O₂ concentration. Experimental results shows that 10 mM H₂O₂ exhibits superior photo-Fenton activity at pH = 2. Mechanistically, in this catalytic system, electron are release from the VB to CB of M.MIL-100(Fe), then it transferred from the CB of M.MIL-100(Fe) to the CB of ZnO and suppressed electron-hole recombination rate on M.MIL-100(Fe) as confirmed by PL analysis. By serving the M.MIL-100(Fe) as a support for ZnO NS, thereby also circumventing the common issue of ZnO aggregation due to its porous nature and high surface area. Additionally, the prepared M.MIL-100(Fe)@ZnO NS reveals outstanding stability and reusability. It is expected that this work not only provide the important role of mesoporous MOF composite for catalytic degradation but also provide handy knowledge to construct more other efficient mesoporous MOF catalysts with different methods and application towards the organic pollutants degradation and to various other fields.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.12.057>.

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